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(54) Title: CAN AND COIL COATING RESINS

(57) Abstract

The invention relates to a can or coil coating resin system. The system contains a mixture of at least 2 polymers wherein at least one polymer has a glass transition temperature greater than 45 °C and wherein the polymers are soluble in organic solvents. The polymer with the glass transition temperature of greater than 45 °C is preferably an amorphous polyester resin. The second polymer may be a resin with a dry solids content between 30% and 100% and a T_g of less than 40 °C.

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CAN AND COIL COATING RESINS

The invention relates to resins which can be
5 used in can and coil coating compositions.

As is evident from the articles 'Pulver-
Bandbeschichten bei 60 m/min' by Dr Graziano (JOT
1996/8, pp. 34-39) and 'Polyester based Powder Coatings
with reference to Coil Coating' by P. Binda (ECCA,
10 Autumn Congress, Brussels, 18-19 November 1996), there
is a need for powder paint systems that can be used in
coil coating processes at application rates of, for
example, 120 m/min. The reactivity of a powder paint
composition is too slow for achieving such high rates.
15 The powder paint application techniques (spraying) are
also too slow in comparison with the roll application
techniques used in can and coil coating processes.
Another drawback is that powder paint layers are
applied as relatively thick layers. Powder paint resins
20 do moreover generally not comply with foodstuffs
legislation. Furthermore, the solid resins having a
high glass transition temperature (T_g) used in powder
paint compositions are not soluble in organic solvents
as used in the coil coating industry.

25 It is the object of the invention to provide
a resin system that can be processed with the aid of
the application techniques currently used on an
industrial scale in the coil coating industry.

The resin system according to the invention
30 is characterised in that the system comprises a mixture
of at least two polymers wherein at least one polymer
has a glass transition temperature greater than about

45°C and wherein the polymers are soluble in organic solvents.

Suitable polymers include for example polyesters and polyacrylates.

5 Preferably the polymers are polyesters.

Preferably, the glass transition temperatures (T_g) of the polymers are different. This difference is generally greater than 5°C.

The molecular weights (M_n) of the polymers are
10 usually between about 2000 and about 15000 and preferably they range between about 3000 and about 8000.

Preferably, the resin having a T_g greater than 45 °C is amorphous.

15 Examples of suitable organic solvents which are used for can and coil coating applications include aromatic hydrocarbon resins (for example the 'Solvesso' types), N-methylpyrrolidone, xylene, propylene glycol monomethylether, methylpropylene glycol acetate,
20 dibasic ester, isophoron, ethyl ethoxypropionate, ethylene-propylene glycol acetate and/or butyl glycol.

Generally, the second polymer has a dry solids content between about 30 % and about 100 %. The T_g of the second polymer is generally lower than about
25 40 °C.

However it is also possible to apply a second polymer having a T_g higher than about 40 °C.

Preferably, the second polymer has a dry solids content of at least 50% and a T_g of less than
30 10°C.

The resins may be linear or branched.

The resin system according to the invention can be applied with the present application techniques

in can and coil coating processing, because the solid high Tg resins dissolve during the preparation of the paint or varnish and can be applied as solvent borne coating paints. The use of these systems implies also
5 low transport costs and less storage volume before the preparation of the paint.

Coatings with specifically desired properties in the wide application range of both can coatings and coil coatings can be obtained by selecting the
10 appropriate choice of the starting resins in the mixture.

To replace a very wide range of different prior art solvent-bearing resins it is only necessary to make a selection from only a few systems according
15 to the invention because the coating properties can be adjusted by changing the mixing ratio between the resins in the mixture.

Another advantage is the possibility of a flexible choice of solvents because the high Tg resins
20 are soluble in a wide range of solvents.

The weight proportion of the polymer having a Tg higher than 45 °C is generally at least 25% and preferably at least 50% (relative to the polymers).

Preferably, the resin system is amorphous
25 because of the desired solubility characteristics.

The polymers are soluble in the organic solvents so that they remain homogeneous and that they show no crystallisation for a period of at least 7 days.

30 Depending on the desired use, the acid numbers of the polyesters range between about 0 and about 100 mg of KOH/gram of resin and the hydroxyl

numbers of the polyesters range between 0 and about 150 mg of KOH/gram of resin.

Systems according to the invention can be used in existing coil coating application lines at rates of up to, for example, 150 m/min and dry layer thicknesses between, for example, 1 and 60 μm .

The polymer mixture according to the invention has to be cured with a crosslinker.

Examples of suitable crosslinkers include compounds containing epoxy groups, compounds containing amino groups and compounds containing isocyanate groups. The crosslinker can be selected depending on the desired use.

Examples of suitable compounds containing epoxy groups are bisphenol A epoxy resins (for example Epikote 828TM, Epikote 1001TM and Epikote 1004TM from Shell), hydrogenated bisphenol A epoxy compounds, aliphatic epoxy compounds, epoxidised alkyd resins, epoxidised oils (for example epoxidised linseed oil or soybean oil), epoxidised borates and triglycidyl isocyanurate. Preferably a bisphenol A epoxy resin is used as an epoxy group containing crosslinker.

The carboxyl : epoxy equivalent ratio is generally between 0.85 : 1 and 1 : 0.85, preferably between 0.9 : 1 and 1 : 0.9.

Examples of suitable amino resin crosslinkers are benzoguanamine, melamine and urea-formaldehyde resins. The polyester : amino resin weight ratio is generally between 95:5 and 60:40 (based on solid resin).

Examples of suitable crosslinkers containing (blocked) isocyanate groups are hexamethylene diisocyanate (HDI), toluene diisocyanate (TDI),

isophoron diisocyanate (IPDI), tetramethylxylene diisocyanate (TMXDI), 3,4 isocyanatomethyl-1methyl-cyclohexylisocyanate (IMCI) and their dimers and trimers. Preferably these crosslinkers are blocked.

5 It is possible to combine the polymers with the same crosslinker. If desired, it is also possible to apply different crosslinkers or mixtures of crosslinkers.

 The resins may contain a solid catalyst fused
10 in it. It is also possible to mix a liquid catalyst or a catalyst solution into the paint formulation comprising the resin mixture.

 Suitable catalysts for acid-epoxy curing are described by Madec et al. in 'Kinetics and Mechanisms
15 of Polyesterifications', Advances in Polymer Science, 182-198 (1985). Examples of suitable classes include N-dialkylamine pyridines, tertiary amines, imidazoles, guanidines, cyclic amines and latent amine catalysts. The catalysts can be blocked if so desired.

20 Examples of suitable catalysts for curing an OH-functional polyester and an amino resin as a crosslinker include strong acids such as sulphonic acids, mono and dialkyl acid phosphate, butyl phosphate and butyl maleate.

25 Suitable sulphonic acids include for example paratoluene sulphonic acid, methane sulphonic acid, nonyl benzene sulphonic acid, dinonyl naphthalene disulphonic acid and dodecyl sulphonic acid.

 Suitable catalysts for curing an OH-
30 functional polyester and an isocyanate based crosslinker include, for example, dibutyl tin dilaureate and zinc octoate.

If catalysts are present, they are generally present in amounts of between about 0.1 and about 5 wt.% (relative to the polyester).

Suitable polyalcohols for preparing the
5 polyesters include ethylene glycol, diethylene glycol, butanediol (1,4), hexanediol (1,6), neopentyl glycol, 2-methyl-1,3-propanediol, 1,3-butanediol, 1,3-propanediol, 1,2-propanediol, 2-ethyl-2-butyl-1,3-propanediol, trimethylpentanediol, hydroxypivalic
10 neopentyl glycol ester, tricyclodecane dimethanol, cyclohexane dimethanol, bisphenol A bishydroxyethyl ether, trimethylolpropane and/or pentaerythritol.

Suitable examples of acids for preparing the polyesters include isophthalic acid, terephthalic acid
15 (dimethyl terephthalate ester), adipic acid, sebacic acid, hexahydroterephthalic acid (CHDA), decane dicarboxylic acid, 5-6-butylisophthalic acid and/or dimerised fatty acids or acid anhydrides such as phthalic anhydride, tetrahydrophthalic anhydride,
20 succinic anhydride, maleic anhydride, trimellitic anhydride, pyromellitic anhydride and/or hexahydrophthalic anhydride.

Preferably phthalic anhydride, isophthalic acid, terephthalic acid and/or adipic acid are used.

25 The esterification reaction preferably takes place under a nitrogen atmosphere at temperatures between 180°C and 260°C. Catalysts such as dibutyl tin oxide, tin chloride, butyl chlorotin dihydroxide (FASCAT™) or tetrabutyoxytitanate and antioxidants such
30 as phosphorous acid, trinonylphenylphosphite or triphenylphosphite can be added as additives. During the reaction the reaction water released is removed through distillation and the desired degree of

esterification can be achieved by applying azeotropic distillation and/or vacuum in the last phase.

The reaction results in a polyester that can be dissolved in an amount of organic solvent or in a
5 mixture of organic solvents such that the desired solids content is obtained. The solvent can be added immediately after the polyester synthesis. The solvent is preferably added during the paint preparation.

Suitable solvents include, for example,
10 aromatic hydrocarbon resins (for example Solvesso types), N-methylpyrrolidone, xylene, propylene glycol monomethylether, methylpropylene glycol acetate, dibasic ester, isophoron, ethylethoxypropionate, ethylene-propylene glycol acetate and/or butyl glycol.
15 Preferably aromatic hydrocarbons and/or butyl glycol are used.

Coil coatings can be obtained via commonly known processes as described for example in 'Coil Coatings' by Joseph E. Gaske (Federation of Societies
20 for Coatings Technology, February 1987, pp. 7-19).

The curing conditions and additives can be chosen to depend on the desired peak metal temperature (PMT) and the nature and thickness of the substrate. The curing time will generally be between about 20 and
25 about 70 seconds at temperatures between about 250°C and about 400°C and a PMT between 204°C and 249°C.

Suitable substrates include for example steel, tin-plated steel and aluminium.

The coil coatings according to the invention
30 are suitable for use as primer and as top coat and can for example be used as coating for household equipment such as fridges, deepfreezes, microwave ovens, ovens

and boilers, as coating for caravans and as coating for facade cladding.

The resin composition according to the invention also yields good results in the can coating industry with which the desired layer thickness generally is thinner and with which the curing conditions differ from the conditions in the preparation of coil coatings.

Can coatings can be obtained via processes of the kind described in for example 'Organic Coatings - Science and Technology, Volume 2: Applications, Properties and Performance' by Z.W. Wicks et al. (Wiley-Interscience, 1994, pp. 284-290).

The curing conditions and additives can be selected to depend on the desired application and the nature and thickness of the substrate. The curing time will generally lie between a few seconds and tens of minutes at temperatures between about 100°C and about 220°C.

Suitable substrates include for example steel, tin-plated steel (ETP, Electrolytic Tin Plate), chromium-plated steel (ECCS, Electrolytic Chromium-Chromium oxide Steel) and aluminium.

The coatings according to the invention are suitable for use as interior and exterior coatings and can be used for example as coatings for beer cans, cans for other beverages ('2 and 3 piece'), spray cans, can ends, tubes, drums, cigar boxes and fish cans (the so-called 'drawn-redrawn (DRD)', 'draw-wall ironed (DWI)' cans). They can be used in pigmented or in unpigmented compositions.

The use of the exterior coating is important primarily from a decorative viewpoint, for giving the

substrate a saleable appearance. It protects the metal from corrosion and the coating also serves as a label.

The interior coating is mainly intended on the one hand to protect the contents of the can against the influences of the metal and on the other to protect the metal against the contents of the can.

The type of monomers to be used to prepare the polyester, the crosslinkers and the curing conditions can be chosen to depend on the desired use.

10 The systems according to the invention can be used in pigmented and in unpigmented compositions.

If so desired, the usual additives such as pigments, fillers, stabilisers, dispersing agents, flow-promoting agents and defoaming agents can be added to the binder system according to the invention.

15 The invention will be elucidated with reference to the following, non-limiting examples.

20 Experiment I

Preparation of a solid polyester resin

294 parts by weight of ethylene glycol, 510 parts by weight of neopentyl glycol, 409 parts by weight of phthalic anhydride, 458 parts by weight of isophthalic acid, 611 parts by weight of terephthalic acid, 1 part by weight of dibutyl tin oxide and 2 parts by weight of trinonylphenylphosphite were heated under a nitrogen atmosphere in a glass reaction flask with a mechanical stirrer, a thermometer and a still with a Vigreux column. The esterification reaction started at 188°C and the reaction water formed was removed through distillation. The maximum reaction temperature was 245°C. After one hour at 245°C this was changed to

vacuum distillation until an acid number of 3.5 mg of KOH/gram was reached.

The acid number of the solid resin obtained was 3.5 mg of KOH/gram and the hydroxyl number was 18.5 mg of KOH/gram.

The viscosity (measured via Emila at 158°C) was 260 dPa.s.

The number average molecular weight (Mn) was 5080 gram/mol, determined with the aid of gel permeation chromatography using a polystyrene standard.

The polyester's glass transition temperature was 50°C (determined with a Mettler TA 3000 DSC (5°C/min.)).

15 Experiment II

Preparation of a high solid polyester resin

301 parts by weight of ethylene glycol, 551 parts by weight of neopentyl glycol, 576 parts by weight of phthalic anhydride, 852 parts by weight of adipic acid and 2 parts by weight of phosphorous acid were heated under a nitrogen atmosphere in a glass reaction flask with a mechanical stirrer, a thermometer and a still with a Vigreux column. The esterification reaction started at 157°C and the reaction water formed was removed through distillation. The maximum reaction temperature was 235°C. After one hour at 235°C this was changed to azeotropic distillation using xylene until an acid number of 5 mg of KOH/gram was reached. This was followed by vacuum distillation until an acid number of 2 mg of KOH/gram was reached. After cooling to 170°C, 857 parts by weight of Solvesso 150™ were added to obtain a 70% dry solids content. The dry solids content is determined by equable applying 0,2

grammes polymer solution on aluminiumfoil (15 x 20 cm).
Next the foil with resin solution is dried during 15
min. in an oven at 150°C. The difference in weight
before and after drying indicates the percentage of dry
5 solids content.

The acid number of the solid resin was 2 mg
of KOH/gram and the hydroxyl number was 20 mg of
KOH/gram.

The viscosity measured in a Physica Viscolab
10 LC3 at 23°C was 73 dPa.s.

The molecular weight (Mn) was 4920 gram/mol,
(determined with the aid of gel permeation
chromatography using a polystyrene standard).

The glass transition temperature of the
15 polyester was -15°C, (determined with a Mettler TA 3000
DSC; 5°C/min.).

Experiment III

20 Preparation of a solid polyester resin

787 parts by weight of 1,2-propylene glycol,
127 parts by weight of trimethylolpropane, 155 parts by
weight of adipic acid, 1092 parts by weight of
isophthalic acid, 465 parts by weight of terephthalic
25 acid, 1.1 parts by weight of dibutyl tin oxide and 1.1
parts by weight of trinonylphenylphosphite were heated
under a nitrogen atmosphere in a glass reaction flask
with a mechanical stirrer, a thermometer and a still
with a Vigreux column. The esterification reaction
30 started at 177°C and the reaction water formed was
removed through distillation. The maximum reaction
temperature was 230°C. After one hour at 230°C this was
changed to azeotropic distillation using Solvesso 150™.

At an acid number of 6.4 mg of KOH/gram vacuum distillation was applied until an acid number of 5.3 mg of KOH/gram was reached.

The acid number of the solid resin was 5.3 mg
5 of KOH/gram.

The glass transition temperature of the polyester was 49°C (determined with a Mettler TA 3000 DSC (5°C/min)).

The molecular weight (Mn) was 5410.

10

Experiment IV

Preparation of a high solid polyester resin

124 parts by weight of ethylene glycol, 468 parts by weight of neopentyl glycol, 213 parts by
15 weight of diethylene glycol, 131 parts by weight of trimethylolpropane, 689 parts by weight of adipic acid, 695 parts by weight of isophthalic acid, 1 part by weight of dibutyl tin oxide and 2 parts by weight of trinonylphenylphosphite were heated under a nitrogen
20 atmosphere in a glass reaction flask with a mechanical stirrer, a thermometer and a still with a Vigreux column. The esterification reaction started at 165°C and the reaction water formed was removed through distillation. The maximum reaction temperature was
25 230°C. After one hour at 230°C this was changed to azeotropic distillation using Solvesso 150™ until an acid number of 0.8 mg of KOH/gram was reached. After cooling to 170°C 857 parts by weight of Solvesso 150™ were added to obtain a 70% solids content.

30 The acid number of the solid resin was 0.8 mg of KOH/gram.

The viscosity, measured with the aid of a Physica Viscolab LC3 at 23°C, was 49 dPa.s.

The glass transition temperature of the polyester was -14°C (determined with a Mettler TA 3000 DSC ($5^{\circ}\text{C}/\text{min.}$)).

The molecular weight (M_n) was 4590.

5

Experiment V

Preparation of a solid polyester resin

546 parts by weight of neopentyl glycol, 106 parts by weight of ethylene glycol, 50 parts by weight of 1,6-hexane diol, 123 parts by weight of 1,4-cyclohexanedimethylol, 65 parts by weight of 1,2-propylene glycol, 1271 parts by weight of isophthalic acid, 146 parts by weight of 1,4-cyclohexanedicarboxylic acid, 1 part by weight of butyl chloroindihydroxide (Fascat 4101™) and 2 parts by weight of trinonylphenylphosphite were heated under a nitrogen atmosphere in a glass reaction flask with a mechanical stirrer, a thermometer and a still with a Vigreux column. The esterification reaction started at 183°C and the reaction water formed was removed through distillation. The maximum reaction temperature was 230°C. After one hour at 230°C this was changed to vacuum distillation until an acid number of 2.4 mg of KOH/gram was reached.

25 The acid number of the resin was 2.4 mg of
KOH/gram and the hydroxyl value was 25 mg of KOH/gram.

The glass transition temperature was 45°C (determined with the aid of a Mettler TA 3000 DSC (5°C/min.)).

30 The molecular weight (M_n) was 4560.

Example I

Paint composition

The polyester according to Experiment I was dissolved in a mixture containing Solvesso 150™, dibasic ester and butyl glycol in a weight ratio of 3:6:1 until a solids content of 50% was obtained. The
5 viscosity was 17 dPa.s (measured at 23°C using a Physica Viscolab LC3). After 3 months at room temperature the resin was still completely dissolved.

To 13.3 parts by weight of the polyester resin thus obtained were added 2.1 parts by weight of
10 anticorrosive pigment (Halox CW491™), 2.1 parts by weight of anticorrosive pigment (Zinkfosfaat ZP/M™), 4.1 parts by weight of an antissettling agent (10% Bentone SD2 in Solvesso 150™), 6.4 parts of titanium dioxide (Kronos 2160™), 10.4 parts by weight of a
15 thinner (Solvesso 150™/butyl glycol 3:1), 0.2 parts by weight of antifoaming/flow-promoting agent (50% Disparlon L1984™ in Solvesso 150™) and 5.0 parts by weight of an extender (Blancfixe Micro). This mixture was then ground to a pigment paste. During the
20 preparation the paste's temperature did not rise above 70°C.

After cooling to room temperature, 7.5 parts of the 50% solution of the resin described above, 2.7 parts of polyester according to Experiment II, 2.8
25 parts of a crosslinker containing amino groups (Cymel 325™), 0.4 parts of catalyst (Nacure 4167™) and 1.2 parts of crosslinker (Epikote 828™) were subsequently added. The mixture was then diluted using a mixture of Solvesso 150™ and butyl glycol in a 3:1 weight ratio
30 until a viscosity of 40-50 seconds' flow time, DIN cup 4, at 23°C (DIN standard 53 211), was reached.

In the following examples the characteristics are determined as follows:

- 1) The solvent resistance test is done by counting the number of dubble rubs (forwards and back) necessary to remove the coating down to the metal. Rubbing is carried out with a piece of cotton wool-soaked in a solvent (methyl ethyl ketone). The result is reported as a number of dubble rubs from 0-100 (numbers above 100 are all reported as > 100).
- 2) gloss: ASTM-D-523
- 10 3) layer thickness: ISO 2360
- 4) adhesion: DIN53151
- 5) appearance: visually
- 6) flow: visually
- 7) T-bend flexibility: ASTM-D-4145
- 15 8) The wedge bend test is conducted to determine the flexibility. A cooled panel (100 mm by 40 mm) is bent over a 6 mm cylindrical mandrel. The folded panel thus produced is then impacted (4,5 Nm) in a device (the wedgebend tester) to form a wedge-shaped contour, flat at one end and 6 mm diameter at the other end. This test piece is then immersed in acidified 3% hydrochloric acid saturated copper sulphate solution for 4 minutes in order to stain any cracks in the coating. The distance in millimeters, which is crackfree is measured. The percentage crackfree is recorded. The higher the % crackfree, the higher the flexibility.
- 25 9) The Erichsen flexibility test evaluates the flexibility of a coating by means of a slow deformation. By means of a slow drawing of a cup from a flat sheet an indication is obtained on how the coating will perform during forming operations in practice.
- 30

The judgement is as follows:

- 1) very bad = total delamination
 - 2) bad = delamination till the top
 - 3) moderate = half of the drawing cup is
5 delaminated
 - 4) good = slight delamination only on the edges
max. 2mm
 - 5) very good = no coating defects.
- 10) The DSM cup flexibility evaluates the ability of
10 the coating to withstand stamping operations that
form a coated flat panel into a DSMR cup.
The judgement of the visual inspection on coating
defects is as follows:
- 1 = very bad
 - 15 2 = bad
 - 3 = moderate
 - 4 = good
 - 5 = very good

20 Example II
Coil coating

The paint according to Example I was applied
to zinc-plated steel (Galfan) as a primer using a 30 µm
wire coater.

- 25 After curing in an oven in a drying cycle of
33 seconds at 358°C (which yields results comparable
with those of coil roll application at 100 m/minute),
resulting in a peak metal temperature (PMT) of 210°C,
the following properties were determined:

- 30 - resistance to solvents: 8 dR
- gloss at 20° 10, gloss at 60°: 45
- layer thickness: 5-7µ
- adhesion in cross-cut tape test: GTO

- appearance: good
- flow: good
- T-bend flexibility: 2.5 T

After a curing cycle of 42 seconds at 358°C,
5 resulting in a PMT of 232°C, a top coat based on a polyester (Uralac SN841™; DSM Resins) applied onto the above primer showed the following properties:

- resistance to solvents: 100 dR
- gloss at 20°: 5, gloss at 60°: 32

10 This shows that a composition according to the invention results in good coil coating properties.

Example III

Paint composition

15 The resin according to Experiment I was dissolved in a mixture consisting of Solvesso 150™ and dibasic ester (1:1 weight ratio) until a solids content of 55% was reached. The viscosity was 40 dPa.s at 23°C, measured according to the ball drop method (Noury
20 vander Lande). 76.6 parts by weight of the polyester thus obtained were mixed with 18.4 parts by weight of the high solid polyester resin according to Experiment II and 5 parts by weight of dibasic ester, resulting in a 'mixpolyester' with a Tg of 32°C.

25 97.5 parts by weight of pigment (Kronos 2310™) and 15 parts by weight of Solvesso 150™ were added to 97.5 parts by weight of the polyester mixture. This mixture was then ground to a pigment paste. During the preparation the paste's temperature did not rise
30 above 70°C. After cooling to room temperature, 18.5 parts by weight of the polyester mixture described above and 14.9 parts of isocyanate crosslinker (Uradur YB147™) were then added. The mixture was subsequently

diluted with Solvesso 150™ to a viscosity of 90-110 seconds' flow time, DIN cup 4 at 23°C (DIN standard 53 211).

5 Example IV
Can coating

The composition according to Example III was applied to an electrolytic tin plate (ETP) using a 40 µm wire coater. After curing in an oven in a drying
10 cycle of 10 minutes at 180°C the following properties were determined:

- resistance to solvents: 17 dR
- appearance: good
- layer thickness: 10 µm
- 15 - DSM cup flexibility: 5/5 (where 1=poor and 5=good), in which the flexibility of a 'DSM-R standard can' was visually determined after punching and sterilisation (demineralised water of 129°C)
- 20 - Erichsen cup flexibility: 5/5 (before/after sterilisation)
- Erichsen cup twice drawn flexibility: 5/5 (before/after sterilisation)
- tap water sterilisation: 5/5
- 25 - wedge bend: 97% crackfree
- adhesion: GTO

Example V
Paint composition

- 30 The polyester according to Experiment V was dissolved in a mixture of Solvesso 150™ and butyl glycol (4:1 weight ratio) to a solids content of 60%. The viscosity was 31 dPa.s at 23°C, (measured with a

Physica Viscolab LC3). The dissolved resin was still stable (clear solution) after 3 months at room temperature.

63.3 parts by weight of the polyester thus
5 obtained were mixed with 31.5 parts by weight of the high solid polyester resin according to Experiment II and 5.2 parts by weight of Solvesso 150TM, resulting in a "mixpolyester" with a glass transition temperature of 18°C and a 60% solids content.

10 To 28.1 parts by weight of the polyester resin mixture thus obtained were added 67.4 parts by weight of pigment (Kronos 2160TM), 15.6 parts by weight of thinner (Solvesso 150TM/butyl glycol 3:1) and 0.4 parts by weight of flow-promoting/dispersing agent
15 (Urad DD2945TM 50% in Solvesso 150TM). This mixture was then ground to a pigment paste. During the preparation the paste's temperature did not rise above 70°C. After cooling to room temperature, 75.6 parts by weight of the 60% "mixpolyester", 15.1 parts by weight of
20 crosslinker (Cymel 303TM, from Dyno Cytec), 4.9 parts by weight of catalyst (Dynapol BL1203TM), 1.03 parts by weight of stabiliser (Tinuvin 292TM), 8.4 parts by weight of a flattening agent (Syloid ED 44TM), 4.4 parts by weight of catalyst (Nacure 2500TM) and 8.4 parts by
25 weight of thinner (Solvesso 150TM/butyl glycol 3:1) were added.

Example VI

Coating composition

30 The composition according to Example V was applied as a top coat onto a coil primer on aluminium using an 80 µm wire coater. After curing in an oven in a drying cycle of 41 seconds at 300°C (which yields

results comparable with those of coil roll application at 100 m/minute), resulting in a peak metal temperature (PMT) of 241°C, the following properties were determined:

- 5 - resistance to solvents: 100 dR
- gloss at 20°: 17, gloss at 60° : 59
- layer thickness: 19 μ
- appearance: good
- flow: good
- 10 - T-bend flexibility: 1T

Example VII

Overprint varnish

The polyester according to Experiment III was
15 dissolved in a mixture consisting of Solvesso 150TM and butyl glycol (4:1 weight ratio) to a solids content of 50%. The viscosity was 35 dPa.s at 23°C, (measured with the aid of a Physica Viscolab LC3). The polyester was still completely dissolved (clear solution) after 3
20 months at room temperature.

68.4 parts by weight of this polyester were mixed with 22.6 parts by weight of the high solid polyester resin according to Experiment III and 9 parts by weight of a mixture of Solvesso 150TM and butyl
25 glycol (4:1 weight ratio), resulting in a 'mixpolyester' with a glass transition temperature of 24°C and a 50% solids content.

To 60.9 parts by weight of the polyester resin thus obtained 8.4 parts by weight of crosslinker
30 (Uramex BF891TM), 5.0 parts by weight of crosslinker (75% Epikote 834TM in butyl glycol acetate) and 18.5 parts by weight of thinner (Solvesso 150TM/isophoron 1:1) were added.

Example VIIICan coating

- 5 The composition according to Example VII was applied to electrolytic tin plate (ETP) as a transparent unpigmented overprint varnish using a 50 μm wire coater. After curing in an oven in a drying cycle of 12 minutes at 185°C the following properties were
- 10 determined:
- resistance to solvents: 5 dR
 - flexibility: DSM cup 5/4 good
 - appearance: good
 - flow: good
- 15 - tap water sterilisation: 5/4.5.

C L A I M S

1. Coating resin system comprising a mixture of at
5 least two polymers wherein at least one polymer
has a glass transition temperature greater than
45°C and wherein the polymers are soluble in
organic solvents.
2. System according to Claim 1, characterised in that
10 the polymers are polyesters.
3. System according to any one of Claims 1-2,
characterised in that the polymer with the glass
transition temperature greater than 45°C is an
amorphous polyester.
- 15 4. System according to any one of Claims 1-3,
characterised in that the second polymer has a dry
solids content between 30 % and 100 %.
5. System according to any one of Claims 1-4,
characterized in that the second polymer has a Tg
20 of less than 40 °C.
6. Can or coil coating composition comprising a resin
system according to any one of Claims 1-5, a
crosslinker and optionally the usual additives.
7. Composition according to Claim 6, characterised in
25 that the crosslinker is a compound containing
epoxy groups, a compound containing amino groups
or a compound containing isocyanate groups.
8. Entirely or partly coated substrate, wherein the
coating is obtained from a composition according
30 to any one of Claims 6-7.

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/NL 98/00193

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C09D167/00

A. The International Search Report is prepared by the International Searching Authority in accordance with the provisions of the Treaty and the Rules and Regulations thereunder.

B. FIELDS SEARCHED

Minimum documentation required for classification followed by classification symbols

IPC 6 C09D

The International Search Report is prepared by the International Searching Authority in accordance with the provisions of the Treaty and the Rules and Regulations thereunder.

Electronic data base consulted during the International Search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 95 01407 A (EASTMAN CHEMICAL COMPANY) 12 January 1995 see page 2, line 7 - line 16; claims 1-11	1-8
Y	EP 0 669 382 A (DSM N.V.) 30 August 1995 see claims 1-8; example II	1-8
A	EP 0 686 678 A (FINA RESEARCH S.A.) 13 December 1995 see claims 1-7	1,3-8
A	EP 0 257 144 A (NIPPON PAINT CO., LTD) 2 March 1988 see claim 1	1-8

☐ Further documents are cited in the continuation of box

☒ Patent family members are cited in annex

Special categories of cited documents

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- L Document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another publication (other special categories specified)
- X Document referring to an invention before, after, or in parallel with the invention
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- X Document member of the same patent family

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